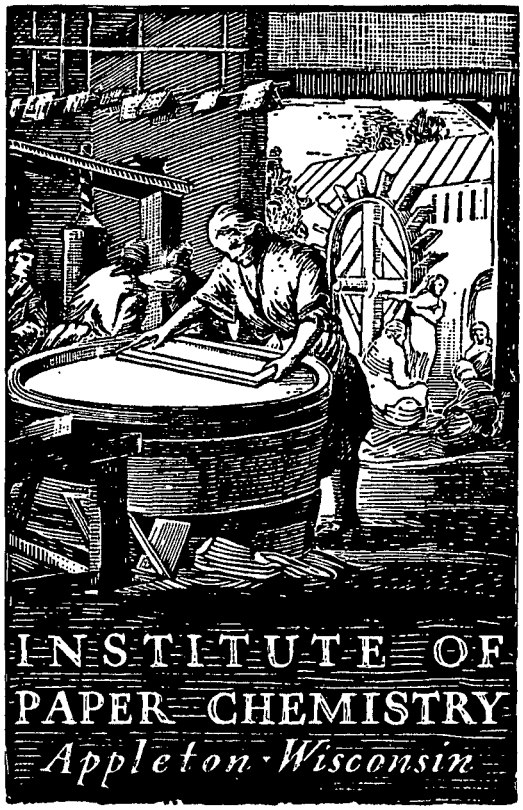

LIGNIN ACTIVATION TO PROMOTE REACTION WITH OXYGEN/ALKALI

Project 3289

Report One

A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 18, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Initial results are reported which have examined the effect of various peracetic acid (PA) pretreatments of red maple (fiberized chip form) on subsequent delignification with oxygen/sodium carbonate (O/A) at high consistency under standard conditions. Three methods of estimating lignin content of the pulps were compared and were found to show the same general trends. Carbohydrate analysis and infrared spectroscopy were used to attempt to characterize the changes occurring during PA pretreatment and O/A delignification. Peracetic acid treatments (pH $\leq$ 7) had a beneficial effect on subsequent O/A delignification when used in amounts of 3-8% (o.d. wood basis). Faster and more selective delignification was promoted. At pH 9, peracetic acid altered the lignin but did not promote its subsequent removal in the O/A step. The results are discussed with reference to known reactions of PA with lignin and related systems. The implications of certain results to possible mechanisms of O/A delignification are also discussed.

INTRODUCTION

BACKGROUND AND OBJECTIVES

This study is related to several other investigations (1-4) currently in progress at the Institute which are focusing on various important aspects of oxidative delignification of wood using oxygen/alkali (O/A). A primary objective of the broad oxidative delignification program is the preparation of commercially attractive papermaking pulps from softwoods and hardwoods in the yield range 80-55%, with TAPPI brightness ranging up to at least 85. In order to achieve this objective, a need was recognized to improve control over carbohydrate degradation reactions that have, in the past, contributed to unsatisfactory pulp strength properties. Thus, in addition to research (1) which is attempting to evaluate various approaches to the desired high-yield papermaking pulps, two other projects (2-3) are seeking an improved understanding of these carbohydrate degradation reactions. The results of these studies may lead to a means of more selective delignification by O/A.

This project is closely related to those mentioned above, but has its main focus on aspects of lignin chemistry. The broad objective of our work is to gain understanding of the impact of lignin structure changes on oxidative delignification by O/A. Specifically, we are investigating pretreatments of both a hardwood and a softwood with limited amounts of selected chemicals to determine (a) which pretreatments will significantly activate lignin to promote subsequent reaction with O/A and (b) whether or not such activation is accompanied by detrimental changes in carbohydrates.

In general, this project seeks means to alter lignin and thereby increase its reactivity to O/A. The rate of lignin removal by O/A depends, in part, on the accessibility of the lignin to the reactive species and on the functional groups

present within the lignin. It is also recognized that important factors include the size of the lignin macromolecules and the size of pores in the cell wall which can resist loss of oxidized lignin fragments above a certain size. It was decided to minimize the accessibility problem by using wood in the form of fiberized chips (1, 5). The main part of our research could then focus on efforts to change the molecular structure (both molecular weight and functional group content) of the lignin and thereby increase its reactivity in the O/A step. A major question then was what changes would be likely to be of value?

The mechanisms responsible for lignin degradation caused by O/A are not well understood. One of the goals of this work is to gain a clearer picture of these important mechanisms. A plausible theory concerning lignin oxidation by O/A has developed from work of Kratzl and coworkers (6-7). The theory, supported by studies of lignin-related model compounds, suggests that a key step in the oxidation process involves ionization of free phenolic hydroxyl groups as shown in Fig. 1. Then in a much slower, possibly rate-limiting step, oxygen (or a related oxidant formed later in the complex system) effects a one electron oxidation of the anion to produce a phenoxy radical. The oxygen would be reduced in this reaction to a superoxide radical ($O_2^{-\bullet}$) which is, itself, a much more reactive oxidant than molecular oxygen.

The phenoxy radicals formed are thought to react further producing cyclohexadienone hydroperoxides, which would in turn ultimately be converted to ring cleavage products.

Kratzl's theory strongly implicates free phenolic hydroxyl groups as important in controlling the rate of lignin oxidation by oxygen/alkali. Some support for this in pulping has come from work of Landucci and Sanyer (8) who examined the influence of several variables on the delignification rate of loblolly

pine by oxygen/alkali. They methylated (diazomethane) a sample of their wood prior to O/A treatment and found the rate of subsequent delignification was only 50% of the delignification rate of unmethylated wood. Presumably, the methylation would predominate on the relatively acidic phenolic hydroxyl groups.

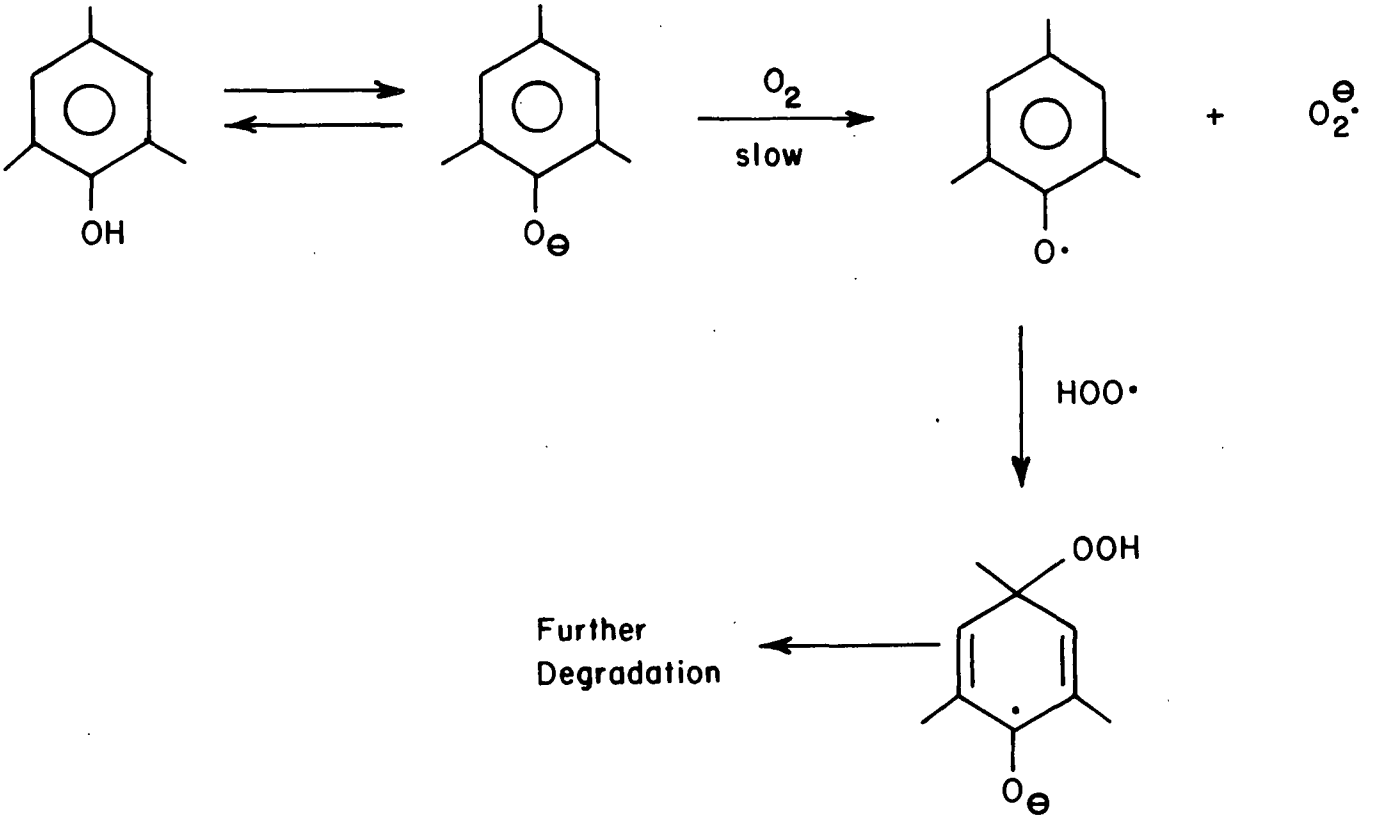

Figure 1. Initial Steps in the Oxidation of Phenolic Groups by Oxygen/Alkali

Another useful concept advanced by Kratzl and coworkers (6-7) is that of relating critical oxidation potentials (COP) to lignin systems. This provides a ranking of phenolic compounds in terms of the relative ease of converting a phenolic hydroxyl group to a phenoxy radical (a one electron oxidation).

$$Ph\text{-}OH \rightarrow Ph\text{-}O\bullet + H^{\oplus} + e^{\ominus}$$

The COP values were determined by potentiometric titration using an inorganic reference system, and they showed that the ease of oxidation is markedly dependent on the nature of other functional groups in the molecule. For example, selected compounds in Fig. 2 show that electron-withdrawing groups (such as carboxyls) on the side-chain increase the COP, i.e., increase resistance to oxidation. Unfortunately, the COP values were determined in aqueous acetone at an apparent pH of 7.45 and the considerable difference in acidities of such phenolic groups in Fig. 2 could greatly hinder the utility of the COP concept. Nevertheless, recent work (6) with oxygen at low alkalinity showed a "rough correlation" between COP and initial rate of oxygen consumption.

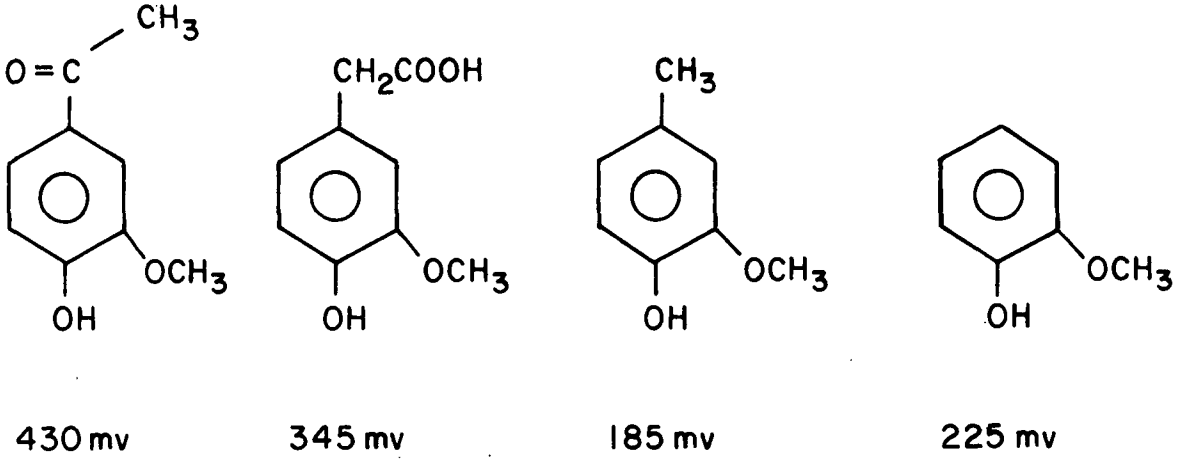

Figure 2. Critical Oxidation Potentials of Some Lignin-Model Compounds

The above theories and considerations, though limited, provide the beginnings of a framework to help design pretreatment experiments which may be beneficial in altering the rate of removal of lignin by O/A. Certainly, the number of free phenolic hydroxyl groups is of considerable interest. A pretreatment which leads to an increase in free phenolics may well promote faster removal of lignin by O/A. On the other hand, a faster rate of formation of phenoxy radicals may result in undesirable concentrations of certain peroxides and possibly superoxide radical ($O_2^{\bar{}\bullet}$) which would lead to more rapid carbohydrate degradation. The probable importance of such intermediates in carbohydrate degradation has been underscored in recent thesis work of Millard (9). Also, Thompson and Corbett (10) found that carbohydrate degradation was related to the amount of oxygen consumed during O/A bleaching of a southern pine kraft pulp.

Thus, the research program must identify ways to increase the rate of removal of lignin by O/A without substantially increasing the rate of carbohydrate degradation if it is to improve the quality of the product.

RESEARCH PROGRAM

As indicated above, it was decided to use wood in the form of fiberized chips as the raw material for this study. The first part of our work has involved red maple exclusively; later emphasis will be given to loblolly pine.

Previous work with selective delignification agents and other work reported in the literature have suggested several pretreatments which may activate lignin to promote reactions with O/A. It appeared to us that the use of selective delignifying chemicals had some worthy advantages. One of these would be that the pretreatment, under milder conditions than commonly used for delignification, would not change the carbohydrates significantly. This would, in turn, simplify interpretation of results after pretreated material was delignified by O/A.

It was decided to concentrate initially on pretreatments using peracetic acid (PA) in part because of its high selectivity toward lignin as indicated by pulping efforts (11-13). Another favorable consideration is the variety of functional group changes that might be achieved using different reaction conditions. Work with lignin-related model systems (14) has shown that PA can react with phenolic ring systems via a probable electrophilic hydroxylation, quinone formation and eventual ring cleavage to muconic acid systems. This is illustrated in Fig. 3. These results on model systems are in accord with studies of chemical changes during PA delignification of wood (15-16). Research in Japan (17-19) has concentrated on reactions of PA with compounds having the β-aryl ether linkage, one of the most abundant links between phenylpropane units in lignin. Again, reaction modes implicated included ring hydroxylation, demethoxylation, quinone production and β-aryl ether cleavage.

The pH of the system during reaction of the wood with PA was thought to be an important variable. The results cited above pertain to acidic media. The course of reactions of PA with lignin at pH values over 7 are quite different from that observed under acidic conditions, as shown by a model system (20) and pulp bleaching (21) studies (where high brightness is achieved with very little lignin removal).

All of the above considerations were taken into account in planning experiments with peracetic acid. It seemed to us that use of a limited quantity of PA as a pretreatment could provide a means of increasing the free phenolic hydroxyl content of the lignin, and that this change might well induce a change in subsequent reactivity to O/A. Alkali-extracted fiberized red maple was used, and the influence of the PA treatment on O/A delignification was examined using O/A delignification conditions recommended on the basis of high consistency work

in a related project (1). Substantial changes in the lignin were thought likely to be reflected in changes after O/A delignification, in pulp yields, lignin and carbohydrate content, viscosity, and possibly rates of oxygen consumption.

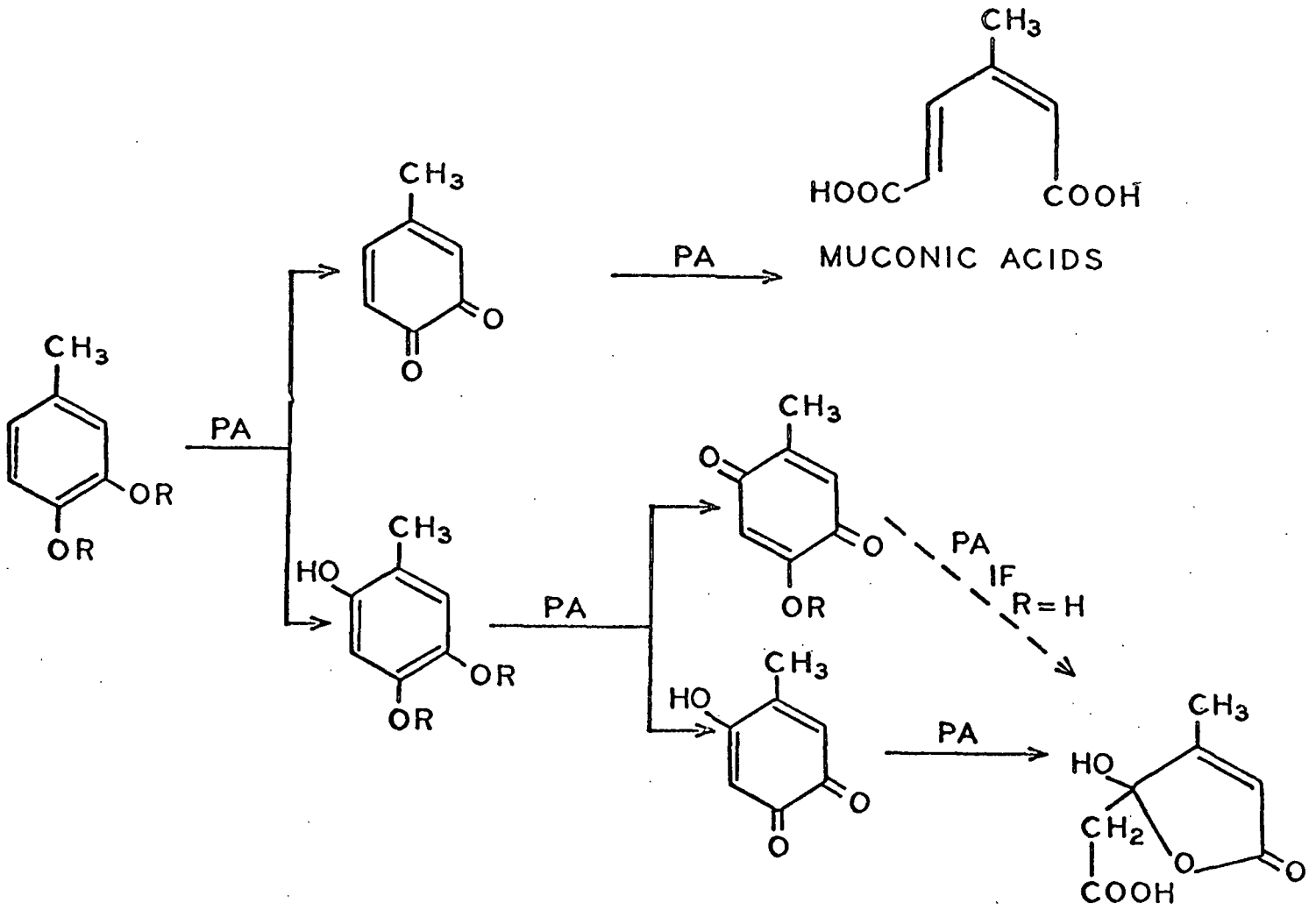

Figure 3. Reactions of Peracetic Acid with Lignin-Model Compounds

One objective was to attempt to characterize, to the extent possible, the chemical changes occurring as a result of the mild chemical pretreatment. Considerable difficulty was anticipated here, and this gave impetus to a related model study in a concurrent thesis investigation (T. E. Crozier) which is examining an isolated dioxane lignin. This thesis seeks to determine the influence of mild PA pretreatments on the structure of the isolated lignin and also the influence of these structure changes on the course of O/A reactions.

This report deals with progress to date on the use of peracetic acid pretreatments to activate lignin. Other limited exploratory experiments have also been done using other pretreatments such as chlorine dioxide, ozone, hydrogen peroxide, sodium dithionite and sodium borohydride. They will be reported later after initial results have been confirmed.

RESULTS AND DISCUSSION

Perhaps the most challenging experimental aspect of this project is the establishment of valid criteria for evaluating results. Many of the traditional methods, which suffer from empiricism, become highly suspect when applied to multi-step processes (e.g., pretreatment followed by oxygen/alkali), particularly where one or more of the steps has not been well-studied. For example, kappa number, which correlates fairly well with lignin content within a series of oxygen pulps (22), may give misleading results when applied to samples where the lignin has been modified by a pretreatment. Therefore, whenever possible, complementary methods were applied to substantiate the results. In addition, an attempt has been made to document some of the chemical changes which occurred in the peracetic acid pretreatments.

EFFECT OF PERACETIC ACID PRETREATMENT ON PULP YIELD

Pulp yield, after constant oxygen/alkali delignification conditions, is not a direct measure of the selectivity of the reactions taking place. A modification of the lignin which made it more reactive would tend to lower pulp yield, giving a pulp with a higher carbohydrate content. On the other hand, a lignin modification which tended to decrease the side reactions resulting in carbohydrate degradation could give a higher yield due to increased carbohydrate retention. Both modifications would have been desirable.

In spite of these drawbacks, pulp yield, which was routinely determined for all samples, provided a convenient method of detecting changes in reactivity as a result of peracetic acid pretreatments. A standard oxygen/alkali cook (4.25 hr, 120°C, 115 psia O_2, 29% consistency) was used to evaluate pretreatments. These conditions were found to give partial delignification, thereby allowing changes in

the extent of delignification to be readily detected. The results are given in Table I.

TABLE I

YIELDS FOR PRETREATMENTS AND OXYGEN/ALKALI COOKS

Sample	Pretreatment % PA[c]	Pretreatment pH	Pretreatment Temp./Time	Pretreatment Yield	O_2 Alk. Yield	Overall[a] Yield
68		none		--	83.6	74.8
76	1(0.6)[b]	4.4	RT/5 hr	99.7	83.8	74.7
79	1(0.6)	7.0	RT/5 hr	100.0	83.2	74.5
100	1.0	9.0	RT/18 hr	99.1	84.5	75.0
179	1.0	9.0	60°/1.3 hr	98.4	82.0	72.3
132	3.8	3.1	RT/24 hr	98.3	81.7	71.9
160	3.0	3.6	60°/4.5 hr	96.2	79.4	68.3
167	3.0	7.0	60°/3.5 hr	96.6	80.5	69.6
145	3.0	9.0	RT/22 hr	96.5	83.5	72.1
177	3.0	9.0	60°/1.5 hr	99.1	81.9	72.7
117	7.8	3.0	RT/23 hr	97.3	77.1	67.1
85	8.0(5.2)	3.6	RT/23 hr	98.8	76.9	68.0
131	10.1	3.0	RT/23 hr	97.4	73.9	64.4
87	8.0(6.6)	7.0	RT/23 hr	99.2	77.2	68.5
118	7.8	7.0	RT/23 hr	91.5	80.0	65.5
95	8.0	9.0	RT/21 hr	98.4	84.9	74.8

[a] Includes 89.5% yield for NaOH treatment of fiberized chips (see Experimental).
[b] Amount consumed in parentheses, if significantly different from applied.
[c] % is on o.d. fiber basis.

Several levels of PA were applied, covering a range of 1-10% on the weight of o.d. fibers. The pH range of 3-9 was studied; the acidic pH's were obtained by simply diluting the PA, and they varied somewhat depending on the extent of hydrolysis to acetic acid during storage of the reagent.

Several patterns emerge from the results given in Table I. Generally, only a small yield loss occurred in the pretreatment step. At levels of greater than 1% peracetic acid applied and at pH ≤ 7, the pretreatment resulted in a lower

yield for the O/A delignification step as well, giving appreciably lower overall yields. This effect is shown graphically in Fig. 4, and is discussed statistically in the Appendix. Although self-decomposition of PA is more rapid at pH 9, an appreciably greater brightening effect was observed in the pretreatment step at pH 9 consistent with other work (20-21) and hence, reactions with lignin must have occurred. However, this did not result in significantly lower overall yields. Changing the pretreatment temperature from room temperature to 60°C appeared to lower the yield somewhat, but additional runs would be required to prove that this trend was significant.

In order to estimate the influence of the sodium carbonate alone (no oxygen) on the yield, control cooks were run employing nitrogen in place of oxygen but otherwise maintaining the same cooking conditions. The yield of a nitrogen/alkali cook of the usual starting material (alkali-extracted fiberized red maple) was 89.5% which can be compared with 83.6% for the corresponding O/A cook (Sample 68, Table I). Similarly, a nitrogen/alkali cook was run using PA-treated fibers (8%, pH 3.7, 24 hours) and the yield was found to be 85.4%. Comparable PA pretreatments (Table I) gave yields of 74-77% in the O/A step; the difference relative to no PA-pretreatment (83.6%) appears to reflect almost entirely a difference in lignin removal (see later discussion).

The PA apparently produces hydrophilic lignin fragments small enough to be removed by hot alkali alone. The decrease in yield, however, in the O/A step can only be partly accounted for in this way, and it appears that PA "activates" lignin to attack by oxygen as well. It should also be recognized that the influence of alkali may be exaggerated in the nitrogen cook because fewer acidic groups would be expected compared with an oxygen cook, and thus less alkali would be consumed.

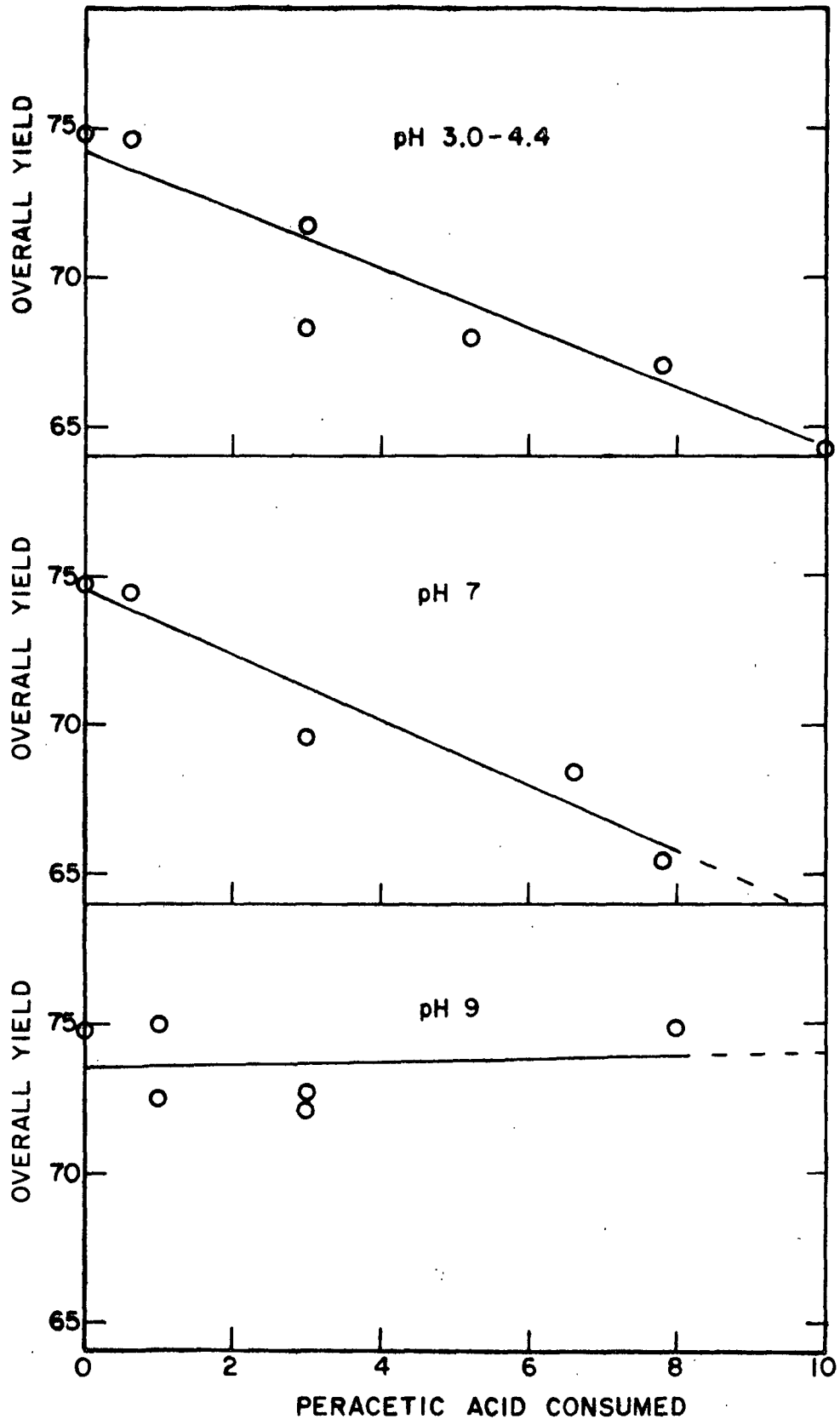

Figure 4. Effect of Peracetic Acid Pretreatment on Overall Yield

The above observations suggest that peracetic acid pretreatment at pH ≤ 7 did have an effect on subsequent delignification with O/A, and therefore, further work was done in an attempt to characterize this effect.

LIGNIN CONTENT OF "PULPS"

The problems involved in using kappa number as a measure of lignin content of samples which have been treated with more than one oxidant have already been mentioned. Nevertheless, kappa numbers were obtained for several samples, and a general trend toward lower kappa numbers at lower pulp yields was observed. In order to get an independent indication of lignin content, carbohydrate analyses (23) were obtained on several of these samples, and lignin was estimated by the difference between 100% and the total yield of alditols after hydrolysis and reduction. Included in the "lignin" from this analysis are sugar acids, acetyl groups, extractives, etc. The results are given in Table II.

The results given in Table II (more detailed data are given in the Appendix, Table IV) become more meaningful if comparison is made with literature values (24) for the analysis of red maple (Appendix, Table V). The "lignin" content given in Table II for red maple is considerably higher than the literature value. However, as mentioned previously, uronic acids, acetyl groups, extractives and ash would be included in this determination by difference. Thus, the value of 35.1 from Table II should be compared with a total of 31.5 from Table V plus an additional 3% extractives (25). The sodium hydroxide treatment caused a 10.5% yield loss, of which 5.6% was aldoses, as shown by the carbohydrate analysis (o.d. wood basis). The remainder of 4.9%, which would be considered "lignin," can be accounted for by partial loss of acetyl and uronic acids, which would be expected in hot alkali. Some loss of extractives would also be expected. Thus, a rigorous

interpretation of the "lignin" values can be misleading. Since, at the lower yield levels, most of the acetyl and uronic acid groups should have been removed, the "lignin" values may be a more accurate measure of the lignin in the pulp. However, it is only below ca. 70% yield that the "lignin" values go below that of the literature value for red maple. This is consistent with the formation of sugar acids during O/A pulping which has been observed previously (26), causing "lignin" to be further inflated.

TABLE II

LIGNIN AND CARBOHYDRATE CONTENT OF PULPS

Sample	Pretreatment % PA	pH	Overall Yield	Kappa	"Lignin"[a] (o.d. Pulp)	Carbohyd. Content (o.d. Pulp)	Carbohyd. Yield (o.d. Wood)
R.M.[b]	--	--	100.0	--	35.1	64.9	64.9
S.M.[c]	--	--	89.5	--	30.4	66.2	59.3
68	--	--	74.8	108	28.2	71.8	53.8
156	(15 hr O_2)[d]		66.8	81	19.8	80.2	53.6
76	1(0.6)	4.4	74.7	112	26.3	73.7	55.1
79	1(0.6)	7.0	74.7	--	27.3	72.7	54.3
100	1.0	9.0	75.0	105	27.3	72.7	54.5
160	3.0	3.6	68.3	84	21.7	78.3	53.5
167	3.0	7.0	69.6	87	22.1	77.9	54.2
164	3.0	9.0	73.5	99	24.9	75.1	55.2
85	8(5.2)	3.5	68.0	71	19.2	80.8	55.5
131	10.1	3.0	64.4	65	14.6	85.4	55.0
87	8(6.6)	7.0	68.5	73	20.6	79.4	54.4
95	8.0	9.0	74.8	85	24.6	75.4	56.4

[a] "Lignin" estimated by difference.
[b] Fiberized red maple.
[c] Starting material (NaOH treated, see Experimental).
[d] O_2/alkali cook under normal conditions, except 15 hr.

Further examination of the data given in Table II reveals that the carbohydrate yield (o.d. wood basis) did not vary a great deal for the samples which were treated with O/A; all samples except one fell in the range of 53.5 to 55.5%, even though the overall yields ranged from 64.4 to 75.0%. Hence, the PA pretreatments did not cause a large overall loss in carbohydrates, nor a large increase in sugar acids. These conclusions are also supported by the generally lower kappa numbers observed for the pulps of lower yields.

In view of the limitations of the carbohydrate analysis as a measure of lignin, it was desirable to evaluate another method for lignin determination. To this end, a modification of the sodium chlorite delignification procedure used for viscosity measurements on high yield pulps (27) was used (see Experimental). The weight loss during this selective delignification was considered a measure of the lignin content of the sample. Table III contains the results, along with the values given earlier for "lignin" and kappa number.

Comparison of the results of chlorite delignification with those obtained from the carbohydrate analysis indicates that, with the exception of three samples, quite good agreement was obtained. This is surprising in light of the earlier discussion which suggested that the carbohydrate analysis gave high values for lignin content. Both methods gave similar slopes in a linear regression analysis with kappa number, and the intercepts suggested that both methods gave high results (assuming permanganate reacts only with lignin) (see Appendix). This is consistent with literature (28) which suggests that chlorite delignification is accompanied by uronic acid degradation.

TABLE III

CHLORITE SOLUBLE LIGNIN, "LIGNIN," AND KAPPA NUMBERS OF PULPS

Sample	Chlorite Soluble Lignin (o.d. Pulp)	"Lignin"[a] (o.d. Pulp)	Kappa
68	26.5	28.2	108
156	21.1	19.8	81
76	25.8	26.3	112
79[b]	24.6	27.3	--
100	26.3	27.3	105
160	20.3	21.7	84
167	22.0	22.1	87
164	25.2	24.9	99
85[b]	25.9	19.2	71
131[b]	18.5	14.6	65
87	19.2	20.6	73
95	24.7	24.6	85

[a] By difference, from carbohydrate analysis.
[b] Samples for which poor agreement between the three methods of lignin estimation was obtained (see Appendix).

SELECTIVITY OF DELIGNIFICATION

It is instructive to consider the analyses on an o.d. wood basis, i.e., carbohydrate yield and lignin yield. Carbohydrate yield is given in Table II and lignin yield can be obtained by multiplying lignin content by overall yield. These results are shown graphically in Fig. 5. This triangle diagram has three axes. The axes are not independent, however, since the carbohydrate and lignin yields must total to the overall yield. The solid line is drawn through the four points (identified in Table II as RM, SM, 68 and 156) which correspond to samples which did not receive PA treatment. It is of interest to note that the line becomes almost parallel to the constant carbohydrate lines at the lower yields, indicating highly selective removal of "lignin." The curvature in the line is indicative of increasing selectivity of the O/A reaction as the yield decreases.

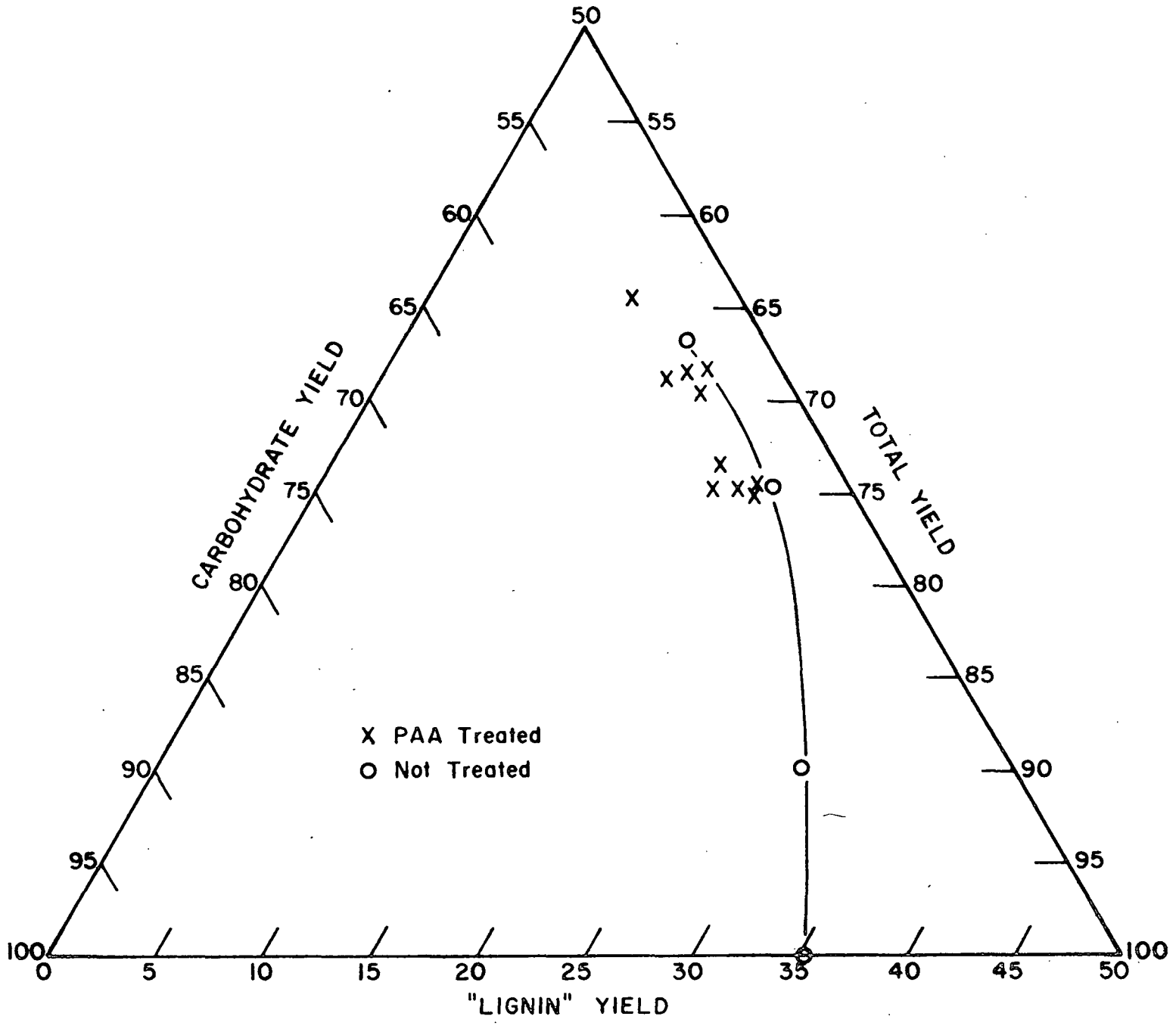

Figure 5. Relationship Between Carbohydrate, Lignin, and Total Yields

The other points on the diagram correspond to PA-treated samples which had been cooked with O/A under conditions identical to those of the third point (74.8% yield) on the curve. They can be identified by reference to Table II. It is of interest to note that all but one of them lie to the left of the curve. This corresponds to a more selective overall delignification. This conclusion must be qualified by the uncertainties associated with the carbohydrate analysis.

In addition to a more selective overall delignification, the PA pretreatment is noted to promote more rapid O/A delignification. An overall yield level of 65-70% can be achieved after PA-treated fibers are cooked (O/A) for the normal 4.25 hour period whereas untreated (no PA) fibers required 15 hours to reach the 67% overall yield level. It should again be noted that this acceleration is not evident for material treated with less than 3% PA.

INFRARED SPECTROSCOPY

Infrared spectra have been obtained for a limited number of materials to try to determine what gross chemical changes resulted from various treatments. Figure 6 illustrates the effect of peracetic acid (8%, pH 3.6) on the alkali-extracted starting material. Peracetic acid caused an increase in carbonyl absorption at 1725 cm^{-1} and a decrease in aromatic ring absorption at 1500 and 1590 cm^{-1}. In particular, the 1500 band has been a useful indicator of lignin content in pulps (29). These spectral differences are consistent with other studies (14-16) which have shown that PA can cleave aromatic rings (involving probable electrophilic hydroxylation) to muconic acids and related structures.

Figure 7 compares the spectra of two oxygen pulps (Samples 68 and 85), one having had no PA pretreatment and the other having been pretreated with 8% PA at pH 3.6. The main difference is in the 1500 and 1590 cm^{-1} bands where it appears

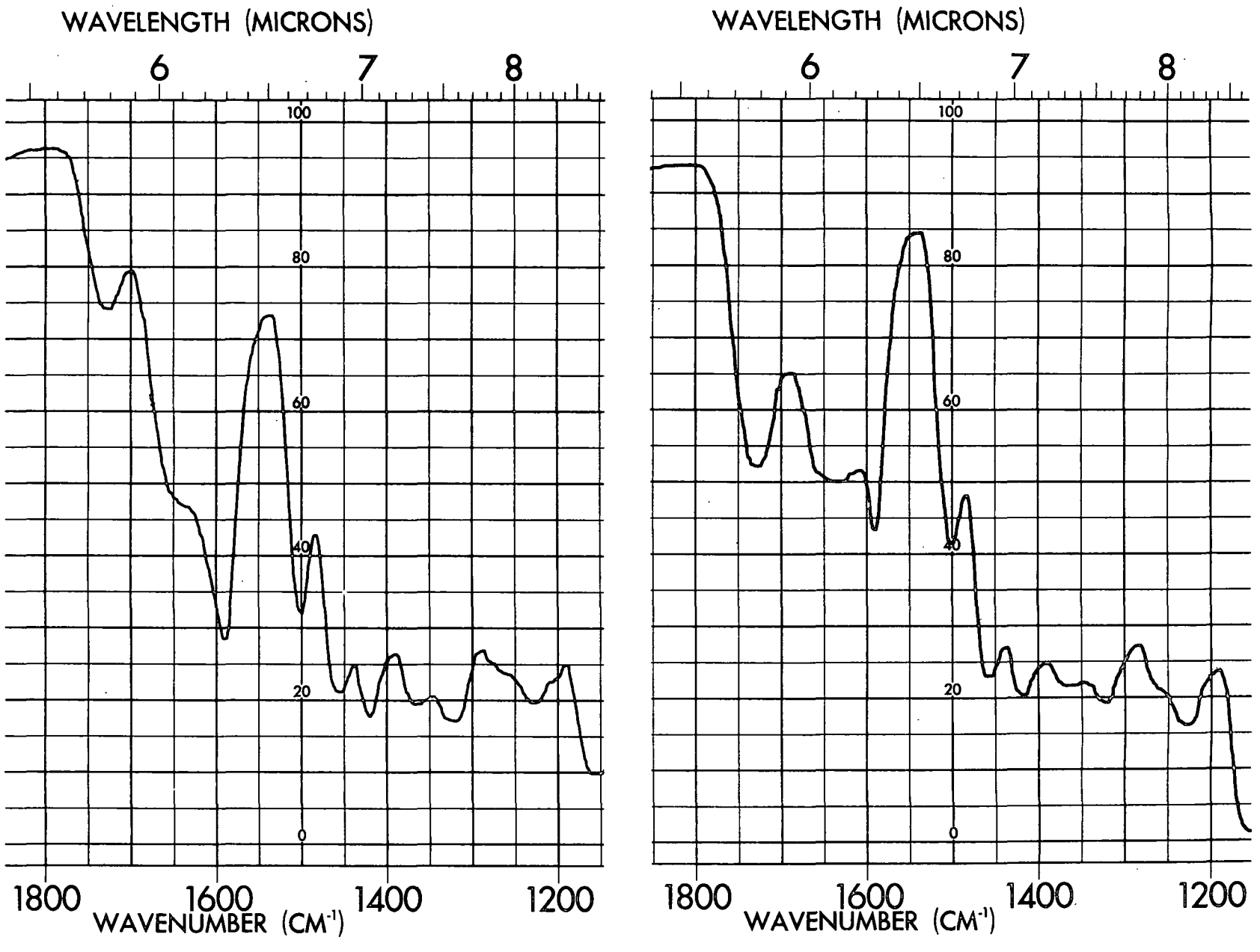

Figure 6. Partial Infrared Spectra of Alkali-Extracted Starting Material Before (Left) and After (Right) Treatment with 8% Peracetic Acid at pH 3.6

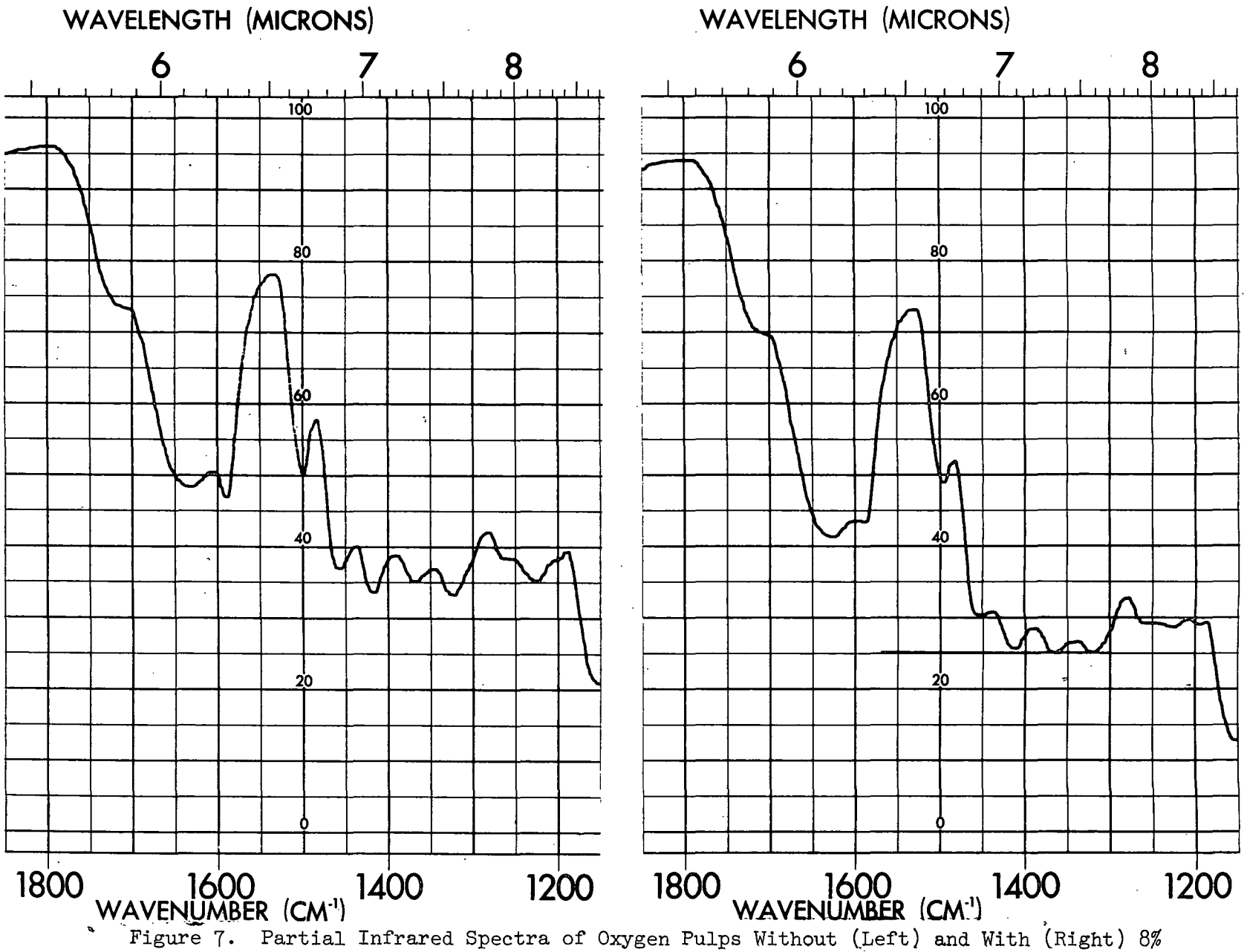

Figure 7. Partial Infrared Spectra of Oxygen Pulps Without (Left) and With (Right) 8% Peracetic Acid Pretreatment at pH 3.6

that fewer aromatic rings are present in the PA-treated sample. It also appears that more lignin removal has occurred in the PA-treated sample, because oxidized lignin residues should be revealed by significant carboxyl absorption (as they are in the PA-treated samples prior to O_2 pulping). In fact, little difference is apparent in Fig. 7 in the 1600-1700 cm^{-1} region where carboxyl and carboxylate groups would show intense absorption.

The spectra in Fig. 8 also indicate that less lignin was removed in the oxygen cook of material pretreated with PA at pH 9 than in the cook of material PA-pretreated at pH 3.6.

Thus, the spectra of the pulps provide a rough estimate of the relative lignin content, and the indications are consistent with other measures of lignin content as discussed earlier. Credibility is somewhat enhanced for the use of kappa number to estimate lignin in oxygen pulps from different treatment sequences.

We have also attempted to detect chemical differences caused by more dilute (1%) PA treatments using infrared difference spectra which proved useful in a previous study of the chlorine dioxide modification of wood (30). The chemical changes, however, at this 1% level appear too subtle to be detected unequivocally.

Although it would be very useful to have an indication of differences in phenolic hydroxyl content for various samples, such hydroxyl groups cannot be readily observed in the infrared due to overwhelming absorbance of alcohol hydroxyl groups.

OXYGEN CONSUMPTION DURING OXYGEN/ALKALI DELIGNIFICATION

A considerable amount of effort was expended in analyzing the gas in the reaction vessel during the reaction with oxygen/alkali. However, due to analytical difficulties, a considerable amount of scatter was experienced in the data and, as

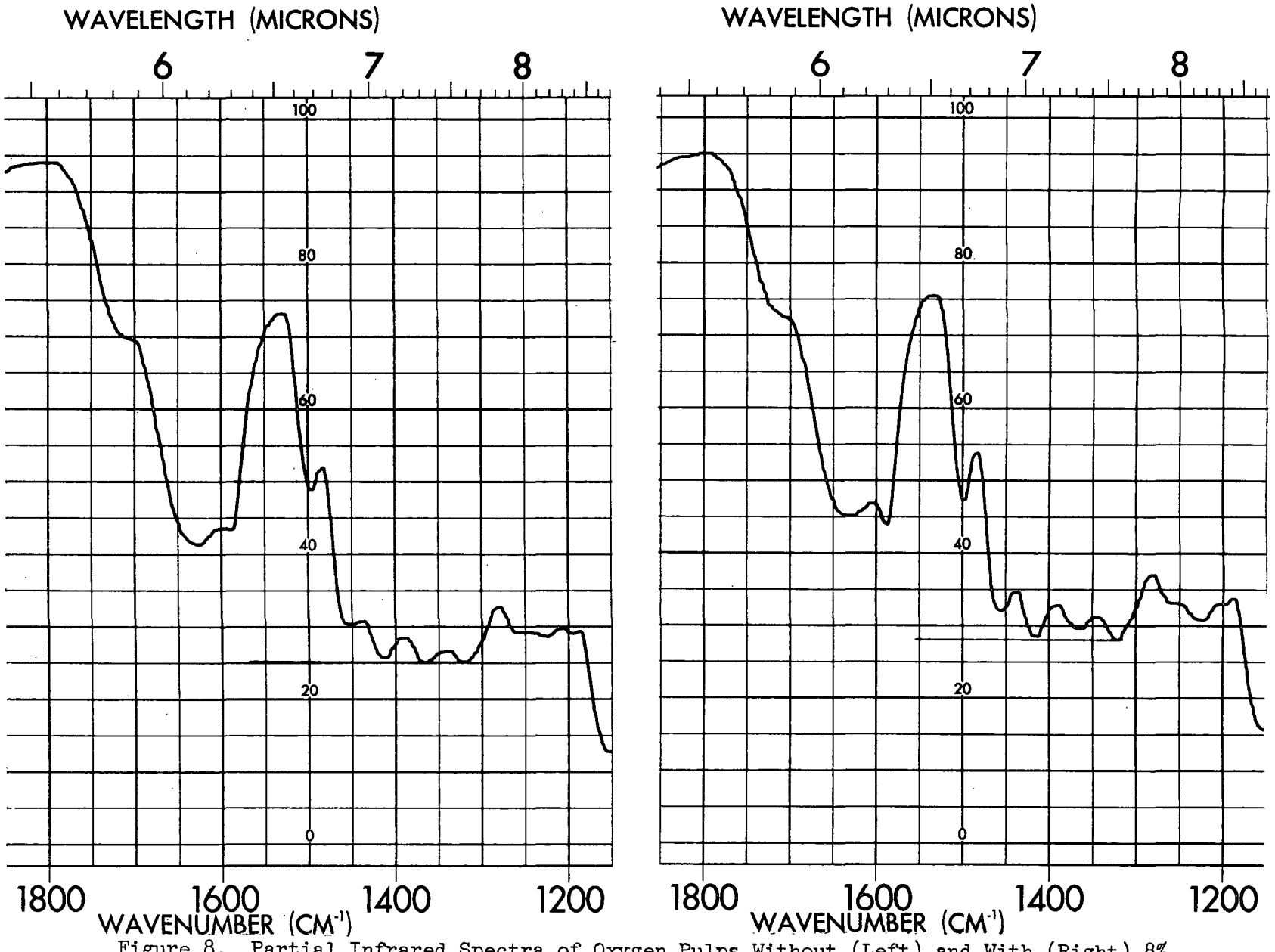

Figure 8. Partial Infrared Spectra of Oxygen Pulps Without (Left) and With (Right) 8% Peracetic Acid Pretreatment at pH 9

a result, no significant trends emerged which allowed conclusions to be drawn about the effect of peracetic acid pretreatment on oxygen consumption. Nevertheless, the results do give a rough estimate of the amount of oxygen consumed in pulping red maple to the yield levels studied in this work.

Figure 9 gives the results of gas analyses for an O/A cook of sodium hydroxide-extracted red maple under the standard conditions of this work (no peracetic acid pretreatment). Using the gas analysis at the end of the cook and the pressure and temperature data, the oxygen consumption amounted to 0.4 gram of oxygen consumed per gram of material removed. If one assumes (incorrectly) that the material removed was lignin with an equivalent weight of 200, this corresponds to approximately 2.5 moles of oxygen per C_9 unit dissolved. As mentioned above, these numbers should be considered only rough estimates and may be quite sensitive to reaction conditions.

IMPLICATIONS CONCERNING THE MECHANISM OF OXYGEN/ALKALI DELIGNIFICATION

An important objective of this work, as cited in the Introduction, is to gain an improved understanding of the impact of lignin structure changes on oxidative delignification by O/A. This necessarily involves consideration of potential mechanisms which may be controlling the course of reactions involving lignin and oxygen. A prime hypothesis suggested by Kratzl's work (6) is that free phenolic hydroxyl groups play an important role in lignin degradation by oxygen. Unfortunately, this is an extremely difficult hypothesis to test in a wood system. A variety of methods for determining phenolic content in lignin have been used; all of them have rather severe limitations and none of them have been used successfully on whole wood (31). Aside from this problem, it is also difficult to change only one type of functional group in lignin.

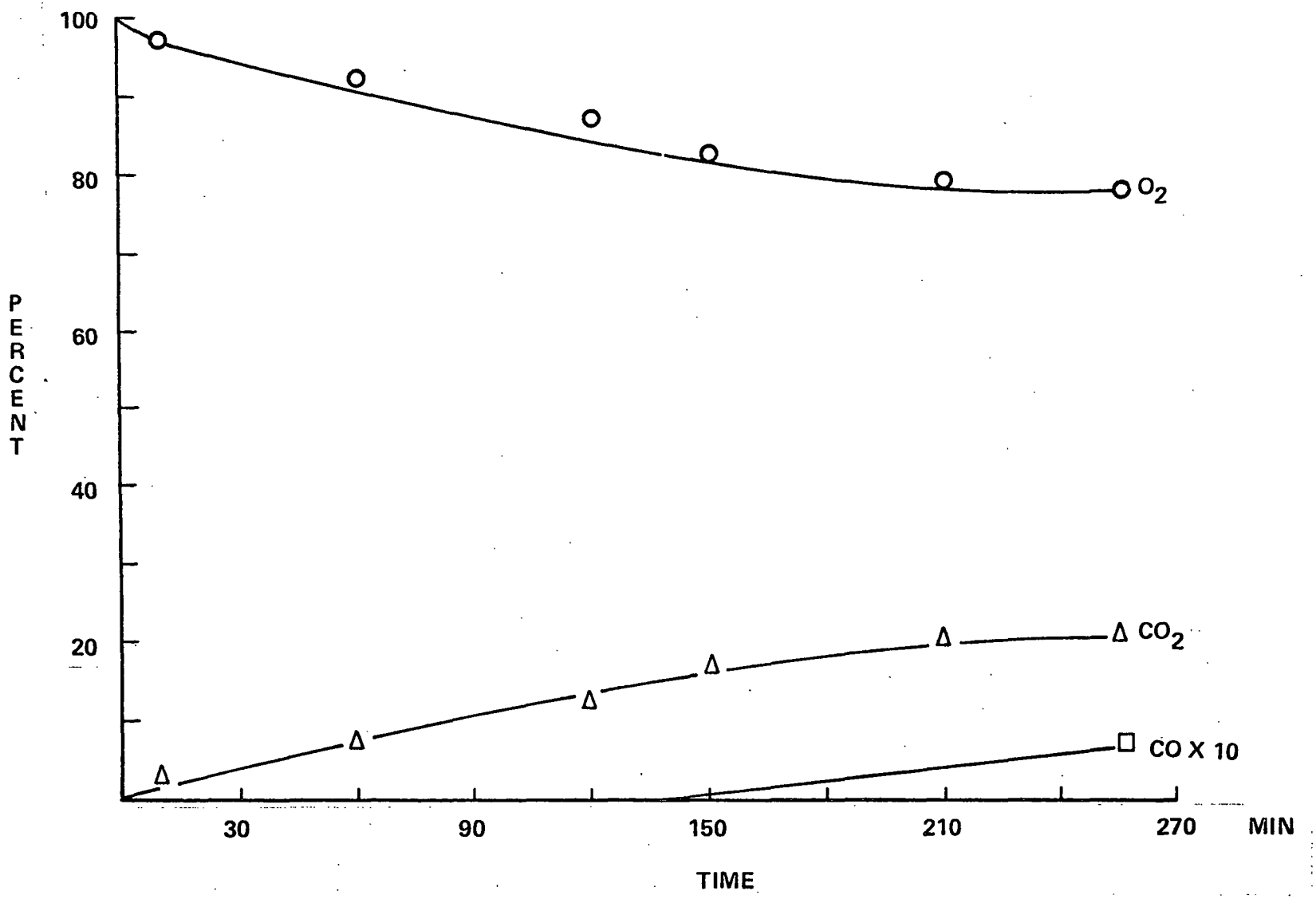

Figure 9. Composition of Gas During Oxygen/Alkali Delignification

It was our hope at the outset that peracetic acid, used in limited amount, might be capable of increasing free phenolic content of fiberized wood and thereby promote faster and more selective delignification by O/A. The desired effect has apparently been achieved, but an excessive amount (considering cost) of PA was found to be necessary. The results, of course, do not prove (nor disprove) that free phenolic groups are critical in the mechanism of O/A delignification. A possible explanation of the results of PA treatments (pH 3-7) is that the PA produces (a) relatively small hydrophilic lignin fragments by degrading a portion of the aromatic rings and cleaving β-aryl ether linkages and (b) aromatic rings containing additional hydroxyl groups which are more reactive to oxygen in the O/A step and thereby more easily solubilized.

Some additional light may be shed on this matter, however, by our results using PA pretreatments at pH 9. Recent work (20,32) has suggested that the brightness gain caused by such treatment is due to a specific attack of peracetic acid on ionized phenolic systems as illustrated for the model compound creosol in Fig. 10. From this work, it seems reasonable to conclude that our PA pretreatment at pH 9 has reduced the phenolic hydroxyl content within the fibers. These fibers were then pulped by O/A, and the resulting yield was about the same as that for fibers which had not been treated with PA. This is a markedly different result from those involving PA treatments at lower pH. The relatively high yield and higher lignin content after the O/A step for the PA (pH 9)-treated fibers may be indirect evidence that free phenolic groups are indeed important to the mechanism of O/A delignification. One might then predict that the loss of these phenolic groups (due to PA at pH 9) could result in a higher yield for the O/A step than that found for O/A pulping of untreated fibers. However, at least two other factors must be recognized; first, our standard pulping times (4.25 hours) appear, in the

case of untreated fibers, to remove only small amounts of true lignin (i.e., a deactivating effect may be undetectable) and second, a degree of lignin fragmentation probably occurs even at pH 9 with PA, and those fragments may well be easily removed by further oxidation in the O/A step.

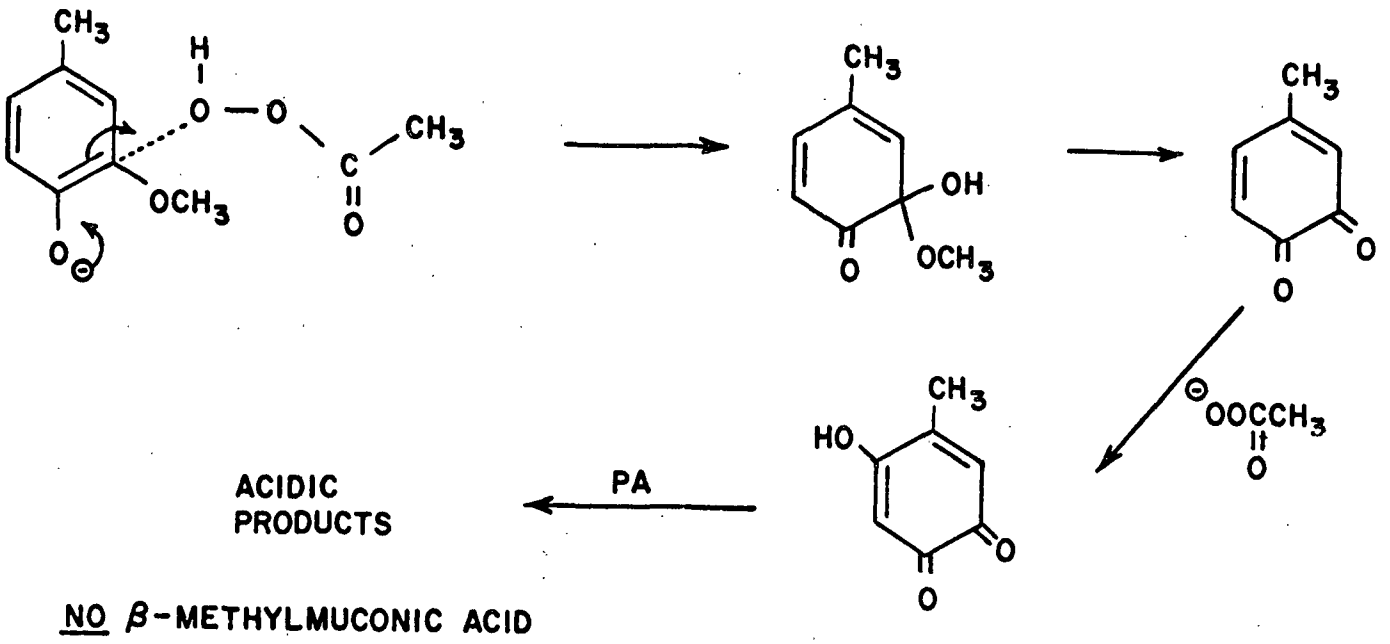

Figure 10. Reactions of Peracetic Acid With Creosol Under Alkaline Conditions

Further experiments will be required to clarify the role of phenolic groups. One such approach, now in progress, will involve methylating the free phenolic groups. The influence of this change will be checked under O/A conditions, but a longer reaction time will be used so that an appreciable amount of lignin in unmethylated fibers is removed. Hopefully, current thesis work (T. E. Crozier) will also help clarify the role of free phenolic groups.

Another question is whether or not carbohydrate damage in the oxygen pulps is significantly affected by the pH used in the PA pretreatment. Work in progress should also answer this.

CONCLUSIONS

Work to date has shown that PA pretreatment definitely had a beneficial effect on delignification of red maple with oxygen/alkali. The reaction with oxygen proceeds faster after 8% PA pretreatment, giving, in 4.25 hours, yields comparable to a 15 hour cook in the absence of PA pretreatment. The delignification with oxygen/alkali also appeared to be more selective after PA pretreatment, giving higher carbohydrate contents at given yield levels. These effects were most noticeable with treatments using more than 6% PA at neutral or acidic pH's.

The peracetic acid pretreatments (pH $\leq$7) increased the carbonyl content and decreased the aromatic content of the material, and these chemical changes, along with presumed changes in the lignin molecular weight and free phenolic content were probably responsible for the increased reactivity to O/A. Increased reactivity to O/A was not noted when PA pretreatments at pH 9 were carried out, and this may be due to a reduction in free phenolic content and a lesser degree of molecular weight reduction in the PA step.

EXPERIMENTAL

GENERAL

Peracetic acid was prepared by acid-catalyzed oxidation of acetic acid with hydrogen peroxide according to a standard procedure (33) which gives material free of sulfuric acid. The product was analyzed by the method of Sully and Williams (34). Kappa numbers were determined in the usual way (35) and carbohydrate analyses were carried out by gas chromatographic analysis of the alditol acetates prepared from the hydrolyzed pulp (23). Gas analyses were determined on samples taken directly from the reaction vessel by syringe, using thermal conductivity gas chromatography (Carbosieve B, 1/8" x 6', 35 to 180°). Infrared spectra were run on KCl or KBr pellets of material which was Wiley-milled and ball-milled according to the method of Vander Linden (30). Samples for Fig. 7 were soaked at pH 4, washed, and air dried prior to sample preparation to eliminate pH effects on the carboxyl/carboxylate ratio.

ALKALINE-EXTRACTION OF FIBERIZED RED MAPLE CHIPS

The equivalent of 300 g o.d. fiberized chips (ca. 60% moisture content) was placed in a Kapax bag along with a thermometer. The fibers were heated in a microwave oven to ∿90°C (5 minutes). A solution of 15 g of sodium hydroxide in 1800 ml of hot distilled water (90°C) was added to the fibers. The weight of the slurry was brought up to 3000 g with additional hot distilled water. The bag was heat sealed and the contents mixed well. The bag was then placed in a hot water bath (90°C) for 30 minutes, during which time its contents were mixed at 10 minute intervals. The fibers were washed with deionized water until the liquor was clear and colorless, centrifuged to remove excess water, and stored in a cold room.

GENERAL PROCEDURE FOR OXYGEN/ALKALI COOKS

The equivalent of 40 g of o.d. fibers (ca. 60% moisture content) was added to a solution of 26.7 g of sodium carbonate in 500 ml of water. The total weight of the solution and fibers was brought up to 800 g with additional distilled water and the fibers were left to soak 30 minutes, after which time enough liquor was filtered off to obtain 29% consistency (138 g). The fibers were hand-fluffed and placed in a teflon basket. The bomb (1000 ml) and shell (Fig. 11) were preheated with steam and the condensate was removed. The basket of fibers was placed into the bomb, which was immersed in an oil bath (120°C). After 15 minutes, the bomb was slowly pressurized with steam up to 24 psig and then released to 14 psig. This procedure was repeated 2 more times over a 5 minute period. The bomb was pressurized with O_2 to a total pressure of 130 psig.(116 psia O_2 partial pressure). The fibers were cooked 4-1/4 hours at 120°C. At the end of the cook, the reaction was stopped by purging the system 2 times with nitrogen while cooling the bomb with water. The fibers were washed with distilled water until the liquor was clear and colorless. Then the fibers were centrifuged, weighed, and stored in a cold room.

NITROGEN (CONTROL) COOKS

Two cooks were run under conditions identical to the oxygen cooks except that nitrogen at the same pressure was substituted for oxygen. The vessel was purged with air prior to heating by pressurization with nitrogen and venting 2-3 times. The workup procedure was the same as in the oxygen cooks.

PERACETIC ACID PRETREATMENT

The equivalent of 60 g of o.d. alkaline-extracted fibers was placed in a 2000-ml Erlenmeyer flask. The desired amount of peracetic acid was mixed

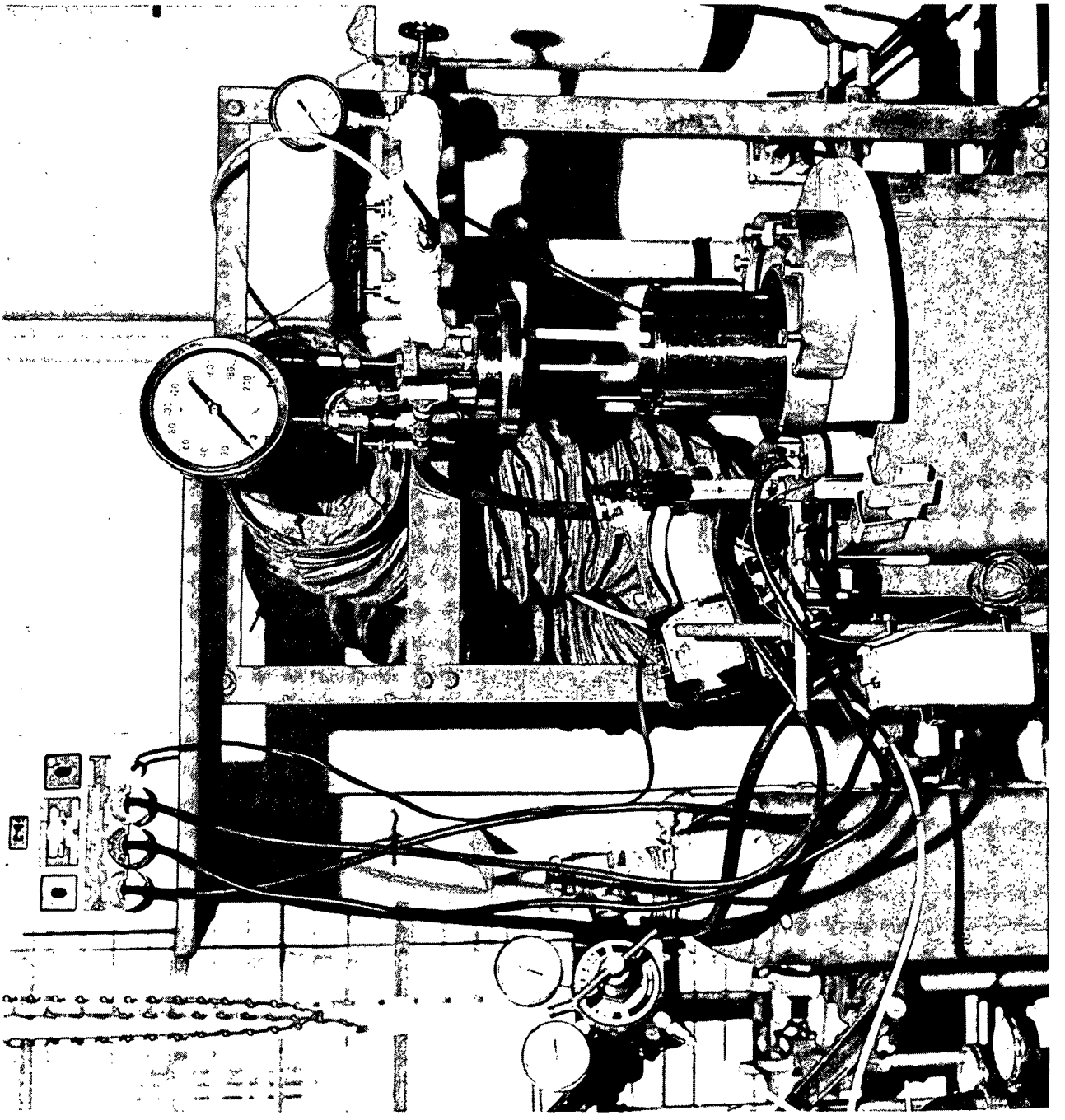

Figure 11. Apparatus Used for Oxygen/Alkali Delignification

with enough distilled water to obain 5% consistency of fibtrs. For solutions at pH 7.0 and 9.0, the pH was adjusted with a Na_2CO_3 solution.

The peracetic acid solution was added to the fibers, the slurry was mixed well and then allowed to stand for the desired length of time and temperature. Room temperature runs were shaken continuously. After the treatment, a sample of liquor was titrated and the fibers were washed with about 1500 ml of distilled water, centrifuged, bagged, and weighed.

SODIUM CHLORITE ($NaClO_2$) DELIGNIFICATION

The procedure is a modification of the method given (36) for the removal of lignin from unbleached pulps prior to viscosity determination. A sodium chlorite solution was prepared by combining 5.0 g of $NaClO_2$, 99 g of distilled water, and 1 ml of glacial acetic acid. The equivalent of 2 g of moisture-free fibers was placed in a large test tube and 20 ml of the $NaClO_2$ solution was added to it and mixed well. The test tube was stoppered and stored in the dark at room temperature with occasional mixing for 24 hours. The recovered pulp was washed well with distilled water and the moisture content and yield were determined.

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APPENDIX

MULTIPLE LINEAR REGRESSION ANALYSIS OF RESULTS

Effect of Peracetic Acid and pH on Yield

The results shown in Fig. 4 suggested that peracetic acid had a similar effect on overall yield under acidic and neutral conditions, and that at pH 9 the effect was different. Therefore, the results were analyzed in several ways, as discussed below.

Since pH did not appear to be a significant variable over the limited range of three to seven, the samples covering that pH range were analyzed by multiple linear regression and the following formula was obtained:

$$\text{Yield} = 74.57 - (1.00 \pm 0.16)\ (\%\ \text{PAA}) + (0.079 \pm 0.28)\ \text{pH}$$

The uncertainties given for the coefficients represent one standard deviation. The T-values indicated that the coefficient for peracetic acid consumed was less than zero at the 95% confidence level and that the coefficient for pH could not be distinguished from zero, in keeping with the initial qualitative observation. The R-squared value was 0.84 for the regression.

Inclusion of the pH 9 samples into the above regression caused pH to become a significant variable, and the following formula was obtained:

$$\text{Yield} = 70.56 - (0.68 \pm 0.21)\ (\%\ \text{PAA}) + (0.49 \pm 0.25)\ \text{pH}$$

The R-squared value, however, dropped to 0.63, since the regression is really not linear in either variable.

The pH 9 samples were considered separately and a linear regression analysis indicated that the yield was independent of the percent peracetic acid consumed

(R-squared = 0.04), as suggested by Fig. 4. This change in behavior is consistent with observations in peracetic acid bleaching.

In summary, over the limited pH range of 3-7, pH is not a statistically significant variable in determining overall yield. Eighty-four percent of the variation in yield can be accounted for by the variation in the amount of peracetic acid consumed. Other variables, which might influence yield, were held constant for this series of experiments. On the other hand, at pH 9, peracetic acid had very little effect on overall yield.

"Lignin," Chlorite Soluble Lignin, and Kappa Number

The relationships between "lignin" content, kappa number, and chlorite soluble lignin were also of interest. Therefore, regression analyses were also done for the results in Table IV, and the following equations were obtained:

$$\text{Chlorite Soluble Lignin} = 10.69 + 0.55 \text{ "Lignin"} \quad (r^2 = 0.59)$$

$$\text{Kappa} = 5.61 + 3.64 \text{ "Lignin"} \quad (r^2 = 0.86)$$

$$\text{Kappa} = 7.78 + 3.42 \text{ Chlorite Soluble Lignin} \quad (r^2 = 0.45)$$

The correlations can be (artificially) improved by omitting the samples noted for giving poor agreement. The equations then become:

$$\text{Chlorite Soluble Lignin} = 2.41 + 0.88 \text{ "Lignin"} \quad (r^2 = 0.89)$$

$$\text{Kappa} = 5.48 + 4.10 \text{ "Lignin"} \quad (r^2 = 0.81)$$

$$\text{Kappa} = 10.57 + 4.40 \text{ Chlorite Soluble Lignin} \quad (r^2 = 0.81)$$

The omission of these values could only be justified by further experiments. However, the second set of equations do tell something about the relationships between the values by the three methods. The relatively small intercept and slope close

TABLE IV

CARBOHYDRATE ANALYSES

(% PAA, pH)	Overall Yield	O.D. Pulp Basis (O.D. Wood Basis)[a] Arabinan	Xylan	Mannan	Galactan	Glucan	Total	"Lignin" (diff.)
R.M.	100.0	0.9	14.9	2.1	0.6	46.47	64.9	35.1
S.M.	89.5	0.8 (0.7)	14.6 (13.1)	2.1 (1.9)	0.4 (0.4)	48.3 (43.5)	66.2 (59.6)	33.8 (30.4)
68 (0%)	74.8	0.6 (0.4)	13.4 (10.2)	1.7 (1.3)	0.4 (0.3)	55.7 (41.7)	71.8 (53.7)	28.2 (21.1)
156 (15 hr)	66.8	0.5 (0.3)	14.1 (9.4)	2.4 (1.6)	0.7 (0.5)	62.5 (41.7)	80.2 (53.6)	19.8 (13.2)
76 (0.6%, 4.4)	74.7	0.5 (0.4)	13.8 (10.3)	1.9 (1.4)	0.4 (0.3)	57.1 (42.7)	73.7 (55.1)	26.3 (19.7)
79 (0.6%, 7.0)	74.7	0.5 (0.4)	13.6 (10.2)	2.0 (1.5)	0.5 (0.4)	56.4 (42.1)	72.7 (54.3)	27.3 (20.4)
100 (1.0%, 9.0)	75.0	0.5 (0.4)	13.3 (10.0)	2.0 (1.5)	0.5 (0.4)	56.4 (42.3)	72.7 (54.5)	27.3 (20.5)
160 (3.0%, 3.6)	68.3	0.4 (0.3)	13.9 (9.5)	2.2 (1.5)	0.7 (0.5)	61.1 (41.8)	78.3 (53.5)	21.7 (14.8)
167 (3.0%, 7.0)	69.6	0.5 (0.3)	13.8 (9.6)	2.1 (1.5)	0.6 (0.4)	60.9 (42.4)	77.9 (54.2)	22.1 (15.4)
164 (3.0%, 9.0)	73.5	0.6 (0.4)	14.0 (10.3)	2.1 (1.5)	0.7 (0.5)	57.7 (42.4)	75.1 (55.2)	24.9 (18.3)
85 (5.2%, 3.5)	68.7	0.4 (0.3)	14.7 (10.1)	2.1 (1.4)	0.6 (0.4)	63.0 (43.3)	80.8 (55.5)	19.2 (13.2)
131 (10.1%, 3.0)	64.4	0.6 (0.4)	15.3 (9.9)	2.6 (1.7)	0.6 (0.4)	66.3 (42.7)	85.4 (55.0)	14.6 (9.4)
87 (6.6%, 7.0)	68.5	0.5 (0.3)	14.1 (9.7)	2.3 (1.6)	0.6 (0.4)	61.9 (42.4)	79.4 (54.4)	20.6 (14.1)
95 (8.0%, 9.0)	74.8	0.6 (0.4)	13.8 (10.3)	2.5 (1.9)	0.7 (0.5)	57.8 (43.2)	75.4 (56.4)	24.6 (18.4)

[a] Carbohydrates calculated as anhydroaldoses.

to 1.0 suggest that the chlorite method and the carbohydrate analysis are measuring approximately the same thing. On the other hand, the negative intercepts in the last two equations suggest that both of these methods are sensitive to material which is not detected by the kappa determination (uronic acids, etc.). Since the intercepts represent large extrapolations, they are probably within experimental error of each other and the negative values are consistent with the apparently high values obtained by these two methods.

CARBOHYDRATE ANALYSES

Total values for carbohydrates were given in Table II for the pulp samples analyzed. However, more complete data are obtained from the gas chromatographic method used, and these data are given in Table IV. For comparison, literature values (24) are given on an extractive free basis in Table V.

TABLE V

COMPOSITION OF RED MAPLE[a]

Glucan	46.6%
Xylan	17.3%
Uronic anhydrides	3.5%
Other carbohydrates	4.6%
Acetyl	3.8%
Lignin	24.0%
Ash	0.2%
	100.0%

[a]Data taken from reference (24).